

## Pervaporation Separation of Isopropanol-Water Mixtures Using Chitosan Based Membranes

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### ABSTRACT

Pervaporation is a method for separating miscible liquids, usually water and organic compounds, using a dense polymeric membrane. The present study investigates the pervaporation performance of homogeneous chitosan membranes for separating water from aqueous isopropanol solution at various conditions. Homogeneous chitosan membranes were prepared from the locally available shrimp shells through various chemical treatments. Firstly, the dried shrimp shells were ground to produce chitin flakes with the average size of 2-6 mm. The decalcification of the chitin produced via treatment with hydrochloric acid was carried out to remove the calcium content. The chitin obtained was subsequently treated in 50 wt. % of sodium hydroxide aqueous solution to remove acetyl groups from chitin to produce chitosan. Homogeneous chitosan membranes were prepared by dissolving preweighed chitosan in acetic acid aqueous solutions. The effects of operating parameters, including feed concentration, feed temperature and downstream pressure on the separation performance of the membrane were investigated. At 30°C and 5 mm Hg downstream pressure, a permeation flux of 48.8 g/m<sup>2</sup>.hr and permeate water concentration of 92.6 wt. % was achieved at a feed water content of 5 wt. %. The temperature dependence of the permeation rate was expressed by an Arrhenius-type relation and with increased of the downstream pressure would led to a reduction in permeation flux.

### INTRODUCTION

Pervaporation is a membrane process for separating miscible liquid mixtures. It is different from others membrane processes, because the membrane constitutes a barrier between the feed in the liquid phase and the permeate in the vapour phase. The solution diffusion mechanism is the most widely accepted model for transport in pervaporation process. The performance of the membrane used to separate a given binary A-B is characterized by the main experimental parameters. The first parameter is the total permeation flux  $J$ , the amount of liquid that is transported through the membrane per unit area and per unit of time. Second, the selectivity in term of separation factor  $\alpha$ , which is defined as:

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B} = \frac{y(1-x)}{x(1-y)} \quad (1)$$

where  $y_A$  and  $y_B$  are the weight concentrations of components A and B in the permeate and  $x_A$  and  $x_B$  are the weight concentrations of the components in the feed. Component A is the more preferentially permeating component in the A/B mixture. The performances of the pervaporation process depend not only upon the physicochemical properties of the polymeric materials and the structure of the membrane but also upon the operating conditons such as feed concentration, feed temperature and downstream pressure.

Since, solubility and diffusivity of the permeating components in the membrane are generally dependent on the operating temperature, pervaporation characteristics in terms of permeation flux also dependent on the temperature. The temperature dependence of the permeation flux can be expressed by Arrhenius-type relationship (Huang and Rhim, 1991):

$$J = J_0 \exp(-E_p/RT) \quad (2)$$

where  $J$  is the total permeation flux ( $\text{kg/m}^2\cdot\text{hr}$ );  $J_0$ , the pre-exponential factor ( $\text{kg/m}^2\cdot\text{hr}$ );  $E_p$ , the activation energy of permeation ( $\text{kJ/mol}$ );  $R$ , gas constant ( $\text{kJ/mol}\cdot\text{K}$ ) and  $T$  the operation temperature ( $\text{K}$ ). Maximum driving force is obtained at zero downstream pressure, so the selectivity is not sensitive at the low downstream pressure but can either increase or decrease at high downstream pressure depending on the relative volatility of the permeating component.

Chitosan was chosen as the membrane material because of its favorable permselectivity and solvent stability, good film forming properties, highly hydrophilic, and good chemical resistant properties (Feng and Huang, 1996; Kubota, 1997 and Mohd. Ghazali, 1997). The present study probes into the possibility of the development of chitosan based pervaporation membranes from domestic shrimp shells. The produced membranes would then be used for pervaporation dehydration of isopropanol/water mixtures.

## MATERIALS

Domestic available shrimp shells were used as the raw material to produce chitosan flakes. Reagent grade sodium hydroxide was purchased from All Chem, ethanol and isopropanol from J. T. Baker, hydrochloric acid fuming 37 % from R & M Marketing and acetic acid from Merck. Deionized distilled water was used in this study.

## EXPERIMENTAL

The dried shells were cut into pieces with an average size of 2-6 mm. The shells were treated with 2 – 3 molar of sodium hydroxide (NaOH) aqueous solution to remove the protein content. The treatments were carried out at 80 – 90°C for 2 hours. Then the shells were washed with distilled water. Furthermore, they were treated in 2 M hydrochloric acid (HCl) aqueous solution at room temperature for 24 hours to remove the calcium from the shells. The chitin were further treated with 50 wt. % of NaOH aqueous solution at temperature of 90 – 110°C for 3 hours in order to remove the acetyl group ( $\text{CH}_3\text{CO}$ ) from the chitin. The flakes obtained by the alkaline treatment were then washed with distilled water, dried under the sun for three hours and further dried up at room temperature. The products obtained are chitosan which were partly deacetylated.

A preweighed quantity of chitosan were first dissolved in 10 wt. % aqueous acetic acid solution at room temperature and stirred them for 24 hours to produce a casting solution consisting of 2 wt. % chitosan. The chitosan aqueous solution was filtered to remove any impurities and undissolved particles to produce a clear homogeneous casting solution by using a vacuum pump. The solution is allowed to settle down for about 3 – 4 hours and the resulting casting solutions were cast onto a petri dish, allowing the casting solution to evaporate at room temperature for 48 hours. The formed membranes were treated in 3 wt. % NaOH solution containing 47 wt. % ethanol, and 50 wt. % of distilled water for 24 hours at room temperature. The membranes were then washed thoroughly with distilled water to remove excess NaOH before being peeled off from the plate and dried at room temperature.

## RESULTS AND DISCUSSION

The total and partial permeation fluxes for isopropanol/water mixtures at 30°C and a permeate pressure of 5 mm Hg (0.67 kPa) are shown in Figure 1. The individual permeant fluxes of the permeating components were calculated from total permeation flux and permeate composition. As the weight percent of isopropanol in the feed increased, the water flux decreased resulting in a decreased in the total flux of the isopropanol /water mixture. However, the amount of water flux was almost equal to the amount of the total flux. Initially the permeate flux of isopropanol increased with the increased of the weight percent of isopropanol in the feed, but from 30 wt. % of isopropanol in the feed onward the isopropanol permeate flux start to decrease gradually.

Figure 2 shows the corresponding data for weight percent of isopropanol in permeate versus the weight percent of isopropanol in the feed solution. Water was the preferential permeate component and it was enriched in permeate product over the whole range of isopropanol/water mixture in the feed. When liquid mixture permeates through a membrane there would be coupling of fluxes (Mulder and Smolders, 1984). The transport of each component in the membrane could be determined by the local concentration of each component of the mixtures. Thus, many investigators suggested that diffusivity of each component in the binary mixture was a function of both concentrations related to the free volume, which in turns depended on the local composition in the ternary system permeant i/permeant j/membrane (Huang and Rhim, 1991).

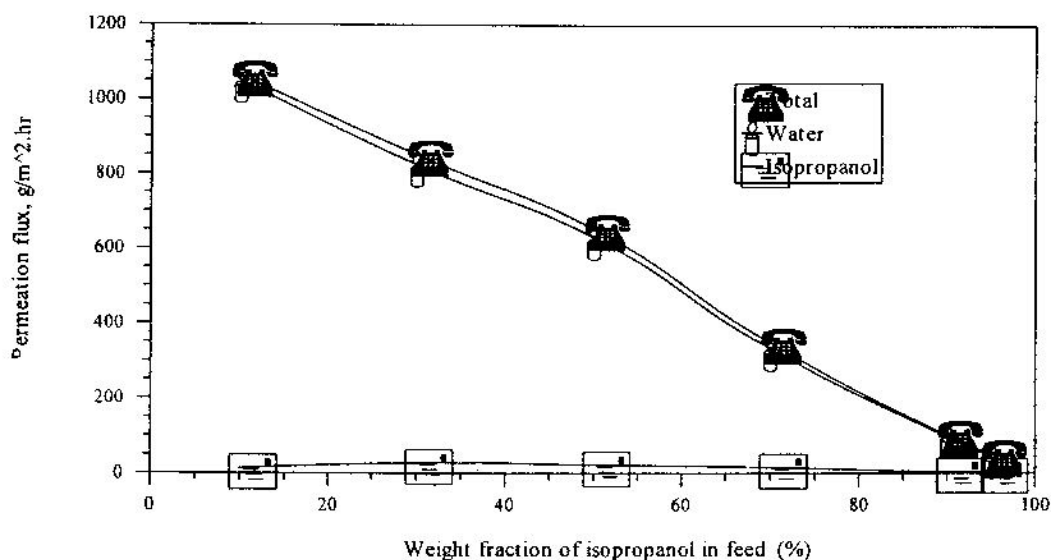


Figure 1: Effect of feed concentration on the individual permeation flux for Homogeneous chitosan membrane. Operating temperature 30°C.

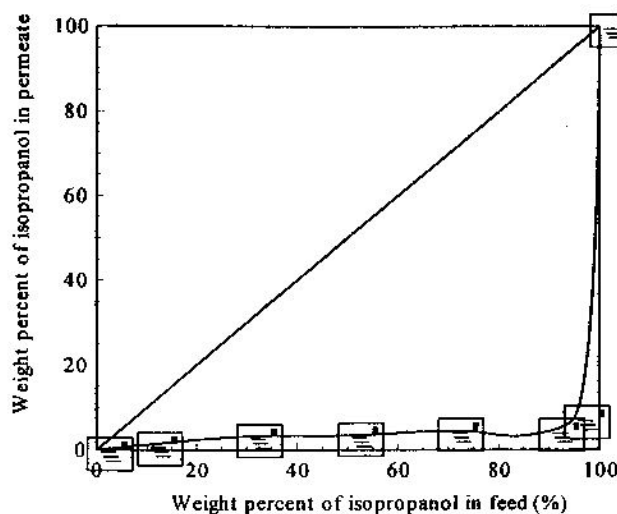


Figure 2: Weight percent of isopropanol in the permeate versus weight percent of isopropanol in liquid feed. Temperature 30°C.

It is suggested that at high weight percent of water in the feed, the plasticizing effect has taken into account in the transport of the permeating components, where the presence of isopropanol enhance the permeation of water. Owing to the high hydrophilicity of the chitosan material, the chitosan membrane would become more swollen at high weight percent of water in feed.

The degree of swelling of the chitosan homogeneous membrane increased with increased in weight percent of water in bulk solution. The swollen membrane would result in less energy required for diffusive transport through the membrane thus making it easier for permeating species to transport through the membrane. On the other hand, the molecular size of isopropanol was bigger than water, so when the free volume increased due to the plasticizing effect, isopropanol would permeate through the membrane. These could be the reasons why at high percent of water in the feed, the membrane showed a high permeation flux and low separation factor. A reverse trend is observed in the low weight percent of water in the feed solution, where a high pervaporation separation factor is accompanied by the low permeation flux as shown in Figure 3.

Figure 4 shows the effects of the downstream pressure on the total permeation flux and water flux for the pervaporation of 90 wt. % of isopropanol in the feed through homogeneous chitosan membranes. From the above result it showed that as the downstream pressure increased from 0.67 kpa (5 mm Hg) to 3.33 kpa (25 mm Hg) the total permeation flux and water permeation flux were progressively reduced. The decreased in the total permeation flux was caused by the decrease in the driving force. Consequently, the decrease in the water permeation flux was due to the more preferential component in this case the water, which was less volatile if compared to isopropanol. Any decrease in water permeation flux would result in the decrease of the separation factor as well.

The total permeation flux for 10 and 90 wt. % of isopropanol in the feed solution are plotted against the reciprocal of the operating temperature in degree Kelvin as shown in Arrhenius plot in Figure 5. The activation energies thus calculated from the slopes for 10 and 90 wt. % of isopropanol in the feed were 15.81 kJ/mol and 21.24 kJ/mol. The results showed that less activation energy was needed in the low weight percent of isopropanol if compared to the high weight percent of isopropanol in the feed solution. The more swollen membrane would require less energy for diffusion of the permeating components if compared to the less swollen membranes. The increased of the feed temperature resulted in a linear increased of the permeation flux.

### CONCLUSION

The domestic shrimp shells could be used as the raw material for the production of high water selective membranes. Isopropanol/water mixtures can be effectively separated by pervaporation through chitosan based membranes. Being hydrophilic, the membranes were highly water selective in the entire range of feed concentration. The pervaporation performances of the chitosan based membranes were effected by the operating parameters such as feed composition, feed temperature and downstream prssure.

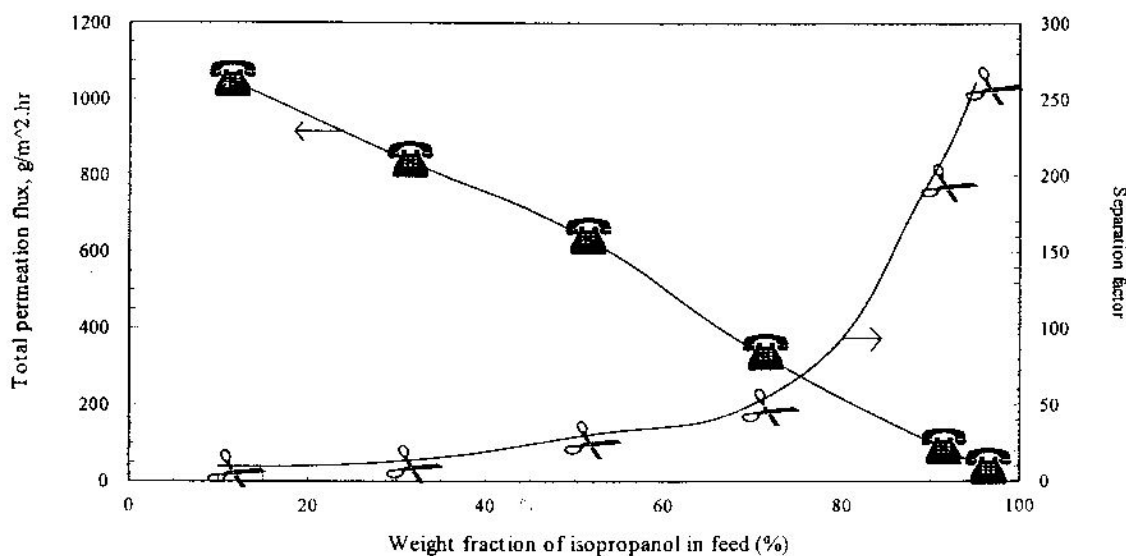


Figure 3: Effect of feed concentration on the separation factor and total permeation flux for homogeneous chitosan membrane. Operating temperature 30°C.

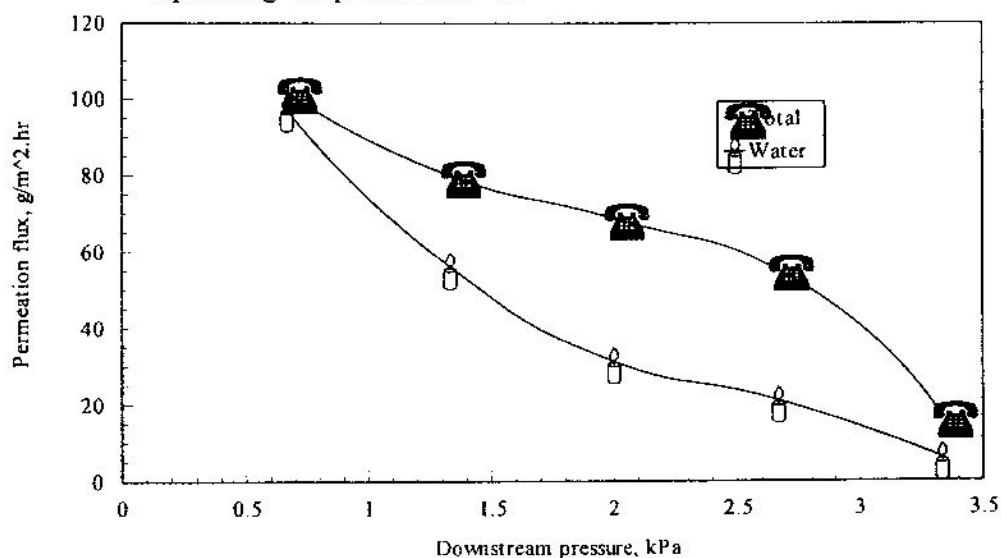


Figure 4: Effect of permeate pressure on total permeation flux and water flux for homogeneous membrane. Feed isopropanol, 90 wt. %. Temperature 30°C.

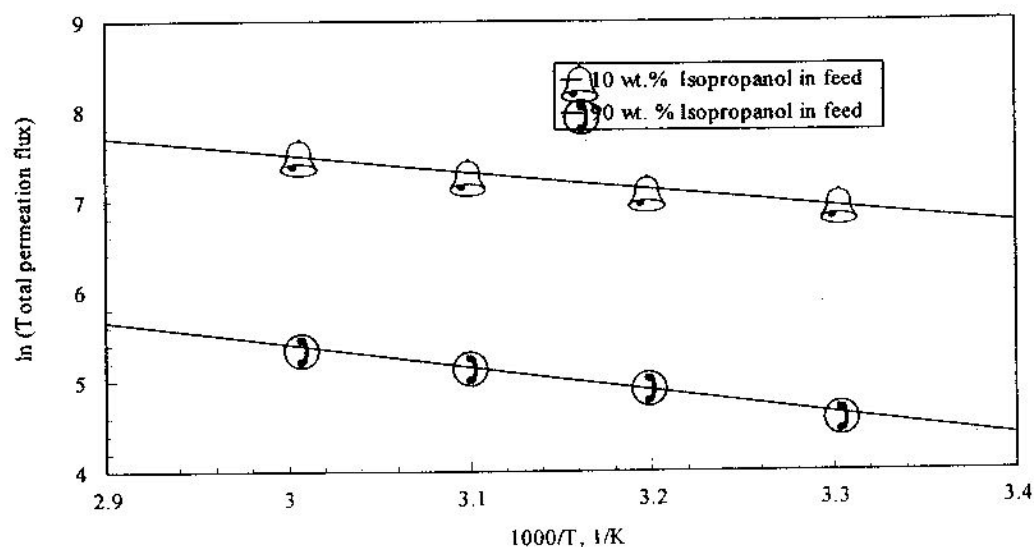


Figure 5: Arrhenius plot of total permeation flux versus temperature.

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